



**JAPANESE PATENT OFFICE
PUBLIC PATENT DISCLOSURE BULLETIN**

**Patent Application Disclosure Number: H6-65123
Disclosure Date: March 8, 1994**

Int. Cl. ⁵	ID Code	File No,	F1	Technology Display Location
C07C 27/00	350	8827-4H		
B01J 23/46	311 X	8017-4G		
C07C 41/50				
43/303		8619-4H		
47/052		7457-4H		

**Application number: Patent Application H4-222884
Filing date: August 21, 1992**

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**A METHOD FOR THE PRODUCTION OF
PARTIAL OXIDATION PRODUCTS OF METHANOL**

Abstract

Purpose: To provide a method for the fabrication of formalin, methylformate, dimethoxymethane, and other compounds that are partial oxidation products of methanol by using methanol and oxygen and by using a novel catalyst consisting of two or more metal components different from an ion conductor.

Constitution: Partial oxidation products of methanol are produced by causing a mixture of methanol and oxygen to come into contact with a novel catalyst consisting of a combination of two or more metals as proton conductors, as a catalyst. In particular, a combination of rhodium and iridium as a metal component being favorable, partial oxidation products of methanol can be produced efficiently by using an additional catalyst consisting of ion conductors such as carbon-based substances and phosphorus-containing films.

CLAIMS

Claim 1 A method for the manufacture of partial oxidation products of methanol, wherein a mixture consisting of two or more metals and/or metal compounds thereof is provided on an ion conductor substance and wherein a mixture of methanol, oxygen, and water is allowed to come into contact with it.

Claim 2 The method of Claim 1, wherein a mixture of methanol, oxygen, and water is allowed to come into contact with a catalyst in which a mixture consisting of metallic iridium and at least one compound selected from iridium compounds, and metallic rhodium and at least one compound selected from rhodium compounds, is provided on an ion conductor substance.

Claim 3 The method of Claim 1, wherein the metal provided on an ion conductor substance and/or the constituent metal of the metal compounds are metals selected from metal groups 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 of the Periodic Table.

Claim 4 The method of Claims 1 and 2, wherein a conducting carbon-based substance is further provided on the ion conductor substance.

Claim 5 The method of Claim 4, wherein the conducting carbon-based substance is one or more substances selected from activated charcoal, graphite, carbon black, and carbon whisker.

Claim 6 The method of Claim 4, wherein the conducting carbon-based substance is a carbon substance pre-treated for oxidation.

Claim 7 The method of Claim 6, wherein the oxidation treatment consists of causing the carbon substance to come into contact, either through heating or at room temperature, in one or more types of solution selected from an aqueous solution of permanganate, an aqueous solution of nitric acid, an aqueous solution of dichromate, and an aqueous solution of sulfuric acid, or the carbon substance is allowed to stand quiescent.

Claim 8 The method of Claim 1, wherein the partial oxidation product of methanol is formalin, methylformate, and/or dimethoxymethane.

Detailed Description of the Invention

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Field of Industry This invention relates to a method for the fabrication of methylformate, dimethoxymethane, and other products which are partial oxidation products of methanol, by using a catalyst made by providing two or more metal species and/or metal compounds thereof on an ion conductor.

0002 Methylformate, dimethoxymethane, and other products which are partial oxidation products of methanol are intermediates in the production of acetic acid, formalin, and other compounds; as such, they are extremely important industrial materials.

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Prior Art A commonly known conventional method for the production of formalin, dimethoxymethane (methylal), methylformate, and other products which are partial oxidation products of methanol involves causing methanol and oxygen to come into contact with each other in the presence of a catalyst. Formalin is commonly produced by using methanol as a raw material and by conducting high-temperature reactions at approximately 500°C in the presence of a silver catalyst and air. Methylal has recently received increased attention as a production raw material for formalin containing a low concentration of water. For example, Patent Application Number H1-287051 and *Chemical Engineering* Vol. 52, p. 411 describe the production of methylal from formaldehyde and methanol through the use of a solid acid catalyst. That method involving the use of formaldehyde as a raw material, however, does not produce methylal directly from methanol; it is an indirect production method from methanol.

0004 As a method for the production of methylformate, *Kokai* Number S 57-2702, *Kokai* Number S 57-26502, and Application Number S 54-12315, for example, describe the production of methylal by the dehydrogenation of methanol at an approximate reaction temperature of 300°C by using a copper-zinc system as a catalyst. Also, Application Number S56-16963 and Application Number S 57-128642 obtain methylformate by causing hydrogen and carbon monoxide to react under high temperature/pressure conditions in the presence of a catalyst, such as copper.

0005 These methods for the production of methylal and methylformate, however, require severe reaction conditions, such as high temperature or high pressure; therefore, they are not production methods involving moderate conditions.

0006 Attempts have been made in recent years to produce various beneficial compounds and simultaneously extract electricity under moderate conditions using a fuel cell system. For example, with regard to the partial oxidation of methanol using a fuel cell system, no methods are known other than the method implemented by the present inventors as described in *Chemistry Letters*, pp. 1945-1948 (1987). The method produces dimethoxymethane (methylal), methylformate, and other products which are partial oxidation products of methanol, by using platinum electrodes in the anode and cathode as catalytic electrodes, and by additionally introducing methanol to the anode side and oxygen to the cathode side. That method, however, required separate supplies of an oxidation-target substance (methanol) as a substance to be introduced to the anode side and an oxidizing agent, such as oxygen, as a substance to be introduced to the cathode side. The method did not allow the presence of an oxidizing agent and an oxidation-target material on a mixed basis, and consequently, it required the prior separation of these substances in order to conduct a reaction. In addition, the method required the isolation of the electrode materials by means of ion-conducting films, which entailed difficulties from an equipment construction standpoint.

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Problems to Be Solved by the Invention The present invention provides a simple method of producing partial oxidation products of methanol under moderate conditions, without requiring the separation of raw material methanol and oxygen, and, in addition, without using complex devices such as fuel cell reactions, thereby solving the problems inherent in conventional

methods, such as the complexity of manufacturing processes, the consumption of a large amount of energy, and low selectivity for partial oxidation products.

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Means of Solving the Problems To solve the problems identified above, the inventors of the present invention studied them diligently. As a result, the inventors discovered an effective, economic method for the production of partial oxidation products of methanol by using, as a catalyst, a catalyst consisting of two or more metal species and/or metal compounds thereof, on an ion conductor, and causing water and methanol, in a mixed state, to come into contact with the catalyst.

0009 Specifically, the present invention is a method for the manufacture of partial oxidation products of methanol, characterized in that it provides a mixture consisting of metals and/or compounds thereof consisting of two or more metal species on an ion conductor substance, and by causing a mixture of methanol, oxygen, and water to come into contact with it. The catalyst used in the present invention is formed by metals and/or compounds thereof consisting of two or more metal species that are substantially different from an ion conductor. Contrast this to the fact that with catalysts that do not use an ion conductor or catalysts comprised of a metal and/or a compounds thereof containing only one metal species and an ion conductor, the progression of reaction is inhibited or the selectivity of partial oxidation products is significantly reduced.

0010 In the present invention, the metals comprising the metals or metal compounds thereof that are used in conjunction with an ion conductor are metals of Groups 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 of the Periodic Table. Specifically, the Group 3 metals include metals that are denoted by element symbols Sc, Y, La, Ac, and so forth; the Group 4 metals are those which are denoted by element symbols Ti, Zr, and Hf; the Group 5 metals are those which are denoted by element symbols V, Nb, and Ta; the Group 6 metals are those which are denoted by element symbols Cr, Mo, and W; the Group 7 metals are those which are denoted by element symbols Mn, and Re; the Group 8 metals are those which are denoted by element symbols Fe, Ru, and Os; the Group 9 metals are those which are denoted by element symbols Co, Rh, and Ir; the Group 10 metals are those which are denoted by element symbols Ni, Pd, and Pt; the Group 11 metals are those which are denoted by element symbols Cu, Ag, and Au; and the Group 12 metals are those which are denoted by element symbols Zn, Cd, and Hg. In addition, when these metals are used as compounds in the present invention, it is recommended that these metals be used as halides, nitrates, sulfates, oxides, hydroxides, phosphates, ammonium salts, acetylacetates, carbonyl compounds, alkyl complexes, ammine complexes, aryl complexes and/or phosphine complexes. In the present invention, a catalyst is formed by providing metals and/or metal compounds consisting of two or more of these constituent metal species on an ion conductor. As noted above, in the method of the present invention, it is essential that the constituent metal species existing on an ion conductor are two or more species.

0011 The Periodic Table referred to in the method of the present invention is the Periodic Table identified in the International Union of Pure and Inorganic Chemistry Nomenclature System (1989).

0012 To facilitate the implementation of the method of the present invention, it is recommended that, during the formulation of the catalyst, a conducting carbon material is mixed

with the metallic components. In addition, the provision of binders in addition to these materials is recommended. The method of the present invention, however, is not limited to these formulation methods.

0013 The carbon substance to be added during the formulation of a catalyst can basically be any carbon substance, provided that it possesses electrical conductivity. Examples of readily available carbon substances include graphite, activated charcoal, carbon black, and carbon whiskers. The method of the present invention is further facilitated by giving an oxidation treatment to these carbon substances prior to mixing them with the metals.

0014 The oxidation treatment of the carbon substances can be carried out by various methods, including the normal heat treatment using an oxygen-containing gas, and a reagent-based oxidation treatment using an acidic reagent. Examples of reagent-based oxidation treatments that can be employed include nitric acid water heat treatment, permanganate aqueous solution treatment, dichromate aqueous solution treatment, and hydrogen peroxide water treatment. The method of the present invention, however, is not limited to these treatment methods.

0015 Further, in the method of the present invention, various binders can be used during the molding of the catalyst. From the standpoint of ease of molding, hot-press molding using teflon resin powder is desirable. It goes without saying, however, that the method of the present invention is by no means limited exclusively to these materials and methods.

0016 Ion conductors that can be used in the method of the present invention include: protonic acids, such as phosphoric acid, sulfuric acid, hydrochloric acid, and nitric acid; solid electrolytes that are known as proton conductors, such as heteropolyacid, H-montmorillonite, and zirconium phosphate; and perovskite solid solutes for which SrCeO_3 is a base material. In addition, a substance can be employed based on a fluorine-containing polymer, such as perfluorocarbon into which one or more cation exchange groups, such as a sulfonic acid group or a carboxylic acid group is introduced, an example being Naflon (a registered trademark of the Du Pont Corporation). Liquids such as phosphoric acid can be used by impregnating them in silica wool or by sandwiching them with an ion-permeable filter or film.

0017 The methanol used in the method of the present invention need not be purified; it can be commonly available reagent-grade methanol. In addition, it can be a mixture with organic substances (saturated hydrocarbons, etc.) other than methanol. While the method of the present invention is implemented by introducing a mixture of these methanol-containing raw materials, water, and oxygen, in this process, methanol and water can be introduced either in a liquid or gas state. When introduced in a liquid state, they can be introduced by diluting them with a solvent for methanol and/or water. When these mixtures are introduced in a gas state, they can be introduced as mixtures of inert gases such as nitrogen, helium, and argon.

0018 According to the method of the present invention, reactions are normally conducted at temperatures from -20°C to 200°C , preferably from 0°C to 100°C . Reactions conducted at an excessively low temperature exact a toll in reduced rates of reaction and require energy for cooling purposes; and reactions that are conducted at too high a temperature cost in a reduced selectivity and require energy for heating purposes; both of which detract from efficiency.

0019 According to the method of the present invention, reactions are normally conducted at normal pressure; however, they can also be conducted with pressurization or under reduced pressure conditions as necessary. The partial oxidation products of methanol, such as methylformate and dimethoxymethane, can normally be separated and purified using distillation and extraction techniques following distillation and condensation from the reaction product liquids or gas, to obtain the desired product.

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Embodiments The following is a more detailed description of the method of the present invention based on embodiments. These embodiments, however, are for illustration only, and the method of the present invention is by no means limited to them.

0021 Embodiment 1

Preparation of a catalyst

(a) Graphite oxidation treatment

Graphite powder was soaked in an 8N aqueous solution of nitric acid. After being heated and boiled for 2 hours, the mixture was thoroughly rinsed with deionized water, dried, and used for the preparation of electrodes.

(b) Preparation of a catalyst

Disc-shaped silica wool (1.0 mm thick, 21 mm in diameter) was soaked in an 85% aqueous solution of phosphoric acid. On the disc, 50 mg of graphite that was oxidation treated with nitric acid, 10 mg of iridium metal powder, 10 mg of rhodium metal powder, and 5 mg of teflon powder were thoroughly blended. After that, a catalyst was prepared by adding and depositing a round sheet of the mixture, 21 mm in diameter, by using the hot-press method.

0022 Embodiment 2

A gas mixture containing methanol (8.3 vol.%), oxygen (40.8 vol.%), and water vapor (50.9 vol.%) was introduced at an 80°C reaction temperature at a flow rate of 34.6 ml/min into a vessel to which the catalyst prepared in Embodiment 1 was attached. As a result, methylformate and dimethoxymethane were produced at rates of 0.67 μ moles/min and 0.73 μ moles/min. In this reaction, carbon dioxide was produced at a rate of 0.36 μ moles/min, suggesting a methanol partial oxidation product selectivity of 67%.

0023 Comparison Example 1

With the exception of the fact that of the catalysts used in Embodiment 2, the ion conductor was removed, and reactions were conducted under conditions all identical to Embodiment 2. As a result, methylformate, dimethoxymethane, and carbon dioxide were obtained at the rates of 2.94 μ moles/min, 0.22 μ moles/min, and 5.37 μ moles/min, respectively, meaning a methanol partial oxidation product selectivity of 36%, and indicating an extreme reduction of partial oxidation product selectivity when compared with Embodiment 1.

0024 Comparison Examples 2 and 3

With the exception of the fact that a sheet, created by hot-pressing, of a 10 mg mixture consisting solely of oxidation-treated mg graphite, 5 mg teflon powder, and iridium or rhodium powder was attached to the disc used in the preparation of the catalyst, reactions were conducted under conditions all identical to Embodiment 2. The results, as shown in Table 1, indicate a virtually complete absence of partial oxidation products of methanol, indicating a 0% selectivity for partial oxidation products.

Table 1

Added metal		Rate of production (μ moles/min)	
	Carbon dioxide	Dimethoxymethane	Methylformate
Iridium	0.09	0	Trace
Rhodium	0.01	0	0

0025 Effects of the invention

The present invention provides the following benefits:

- (1) Partial oxidation products of methanol can be produced under highly moderate conditions with a high degree of selectivity.
- (2) Partial oxidation products of methanol can be produced highly economically using an exceedingly simple apparatus and a simple process.
- (3) Reactions can be conducted in a mixture, without requiring the prior separation of methanol, water, and oxygen, and partial oxidation products of methanol can also be produced easily from a process standpoint.

Thus, the present invention is a production method for partial oxidation products of methanol offering several advantages.

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